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Chemistry of Unsaturated Group 6 Metal Complexes with Bridging Hydroxy and Methoxycarbyne Ligands. 3. Formation and Cleavage of C−C and C−O Bonds in the Reactions of the Complexes $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}COR)(\mu\text{-}PCy_2)]BF_4$ (R = Me, Et)

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The reactions of the 30-electron complexes $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}COR)(\mu\text{-}PCy_2)]BF_4$ (Cp = $\eta^5\text{-}C_5H_5$; R = Me, Et) with CO, CN^tBu, or tetraethylpyrophosphite (tedip) lead to the new 32-electron complexes $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(OMe)C(OR)\}(\mu\text{-}PCy_2)(CO)_2]BF_4$, $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(OMe)C(OMe)\}(\mu\text{-}PCy_2)(CN^tBu)_2]BF_4$, and $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(OMe)C(OMe)\}(\mu\text{-}PCy_2)(\mu\text{-}tedip)]BF_4$, respectively. These products contain a bonded dialkoxyacetylene molecule resulting from the coupling of two alkoxycarbyne ligands, induced by the addition of the donor molecules to the unsaturated dimetal center of the starting material, and this coupling can be fully reversed in the dicarbonyl product upon photochemical treatment. The structure of the diisocyanide and tedip complexes, both displaying quite short intermetallic lengths (ca. 2.66 Å), was confirmed crystallographically. The structure of the dicarbonyl derivative, which in solution exhibits *cis* and *trans* isomers, was optimized using DFT methods, which also led to the prediction of short intermetallic distances (2.75 Å). Demethylation of the dicarbonyl complexes leads to the new carboxycarbyne derivatives $[Mo_2Cp_2\{\mu\text{-}C(CO_2R)\}(\mu\text{-}PCy_2)(CO)_2]$ (R = Me, Et) as a result of the unexpected 1,2-shift of the methoxyl group occurring in the ketenyl intermediate (not detected) presumably formed first. This proposal is supported by DFT calculations, these predicting a moderate activation barrier ($\Delta G^{\ddagger}_{298} = 78$ kJmol^{-1}) for the spontaneous transformation ($\Delta G_{298} = -51$ kJ mol^{-1}) of the ketenyl intermediate into the carbyne complex finally isolated. The bis(methoxycarbyne) complex is also reactive toward the 16-electron fragment $Ru(CO)_4$, to give the 46-electron cluster $[Mo_2RuCp_2(\mu\text{-}COMe)_2(\mu\text{-}PCy_2)(CO)_4]BF_4$, which concentrates most of its electronic unsaturation at the dimolybdenum center (Mo−Mo = 2.686(1) Å), in spite of the rearrangement of the carbyne ligands, both of them now bridging one of the Mo−Ru edges, according to an X-ray diffraction study.

Introduction

Recently we have described full details of the synthesis and electronic structure of the unsaturated bis(alkoxycarbyne) cationic complexes $[Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}COR)(\mu\text{-}PCy_2)]BF_4$ [R = Me (**1a**), Et (**1b**)].[1] A preliminary study on the bis(methoxycarbyne) complex **1a** had revealed that this unsaturated cation might experience unusual transformations involving the formation and cleavage of C−C or C−O bonds under very mild conditions.[2] In particular, a rare coupling between methoxycarbyne ligands could be induced on **1a** by the double addition of two-electron donor molecules, to give the alkyne-bridged complexes $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2(OMe)_2\}(\mu\text{-}PCy_2)(L)_2]BF_4$ [L = CN^tBu (**2**), L = CO (**3a**)]. Interestingly, the coupling process leading to compound **3a** could be fully reversed through photochemical decarbonylation, to regenerate compound **1a** quantitatively.[2] While there are several reports of carbyne−carbyne coupling reactions yielding coordinated alkynes or the reverse,[3] rarely have these processes been found involving alkoxycarbyne ligands,[4] or being reversible. In fact, we can quote only two previous examples of reversible coupling between carbyne ligands of any type, these occurring at the Fe_3 or Fe_4 metal centers of the complexes $[Fe_3(\mu\text{-}CCH_3)(\mu\text{-}COEt)(CO)_9]$[5] and $[Fe_4(\eta^5\text{-}C_5H_4Me)_4(\mu\text{-}CH)_2(\mu_3\text{-}CO)_3]$,[6] these being triggered through carbonylation and two-electron reduction, respectively. Moreover, the behavior of the dimethoxyacetylene complex **3a** was also unusual in yielding the carboxycarbyne complex $[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ upon demethylation, this implying the occurrence of an unexpected 1,2-shift of the OMe group.[2] We thus decided to study these unusual transformations in more detail. We have noted previously that the study of the reactivity of hydroxy- and alkoxycarbyne ligands at unsaturated binuclear centers might also be of interest in the context of metal-catalyzed hydrogenation of CO under either homogeneous or heterogeneous conditions.[7] In this context, our preliminary results on the reactivity of complex **1a** were relevant since for the first time they suggested that the C−C coupling

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(1) García, M. E.; García-Vivó, D.; Ruiz, M. A.; Aullón, G.; Alvarez, S. *Organometallics* **2007**, *26*, 4930.

(2) Alvarez, C. M.; Alvarez, M. A.; García, M. E.; García-Vivó, D.; Ruiz, M. A. *Organometallics* **2005**, *24*, 4122.

(3) (a) Shapley, J. R.; Comstock, M. C. *Coord. Chem. Rev.* **1995**, *143*, 501. (b) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127. (c) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

(4) (a) Bronk, B. S.; Protasiewicz, J. D.; Pence, L. E.; Lippard, S. J. *Organometallics* **1995**, *14*, 2177. (b) Wen-Yann, Y.; Shapley, J. R. *J. Organomet. Chem.* **1986**, *315*, C29. (c) Nuel, D.; Daham, F.; Mathieu, R. *J. Am. Chem. Soc.* **1985**, *107*, 1658.

(5) Nuel, D.; Daham, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436.

(6) Okazaki, M.; Ohtani, T.; Ogino, H. *J. Am. Chem. Soc.* **2004**, *126*, 4104.

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reactions in the Fischer–Tropsch synthesis might occur (even if as a side pathway) at only two metal centers and without the involvement of fully hydrogenated (CH_x) surface species, via hydroxycarbyne derivatives. However, although hydroxycarbyne ligands have been suggested as possible intermediates in carbon monoxide hydrogenation,[8] we still note that no experimental evidence of their formation in the real catalytic systems has yet been found.

In this paper we report full details of our study on the reactions of the unsaturated cations **1a**,**b** toward simple donor molecules to give alkoxyalkyne-bridged derivatives. This has been complemented with density functional theory (DFT) calculations on the carbonyl derivatives, to gain a better understanding of the reversibility of the C−C coupling between alkoxycarbyne ligands so induced. Full details of the demethylation reactions of the alkoxyalkyne-bridged complexes are also included, these being in turn complemented by DFT calculations of the corresponding reaction profile, here involving the unexpected 1,2-shift of a methoxyl group at an unstable ketenyl intermediate.

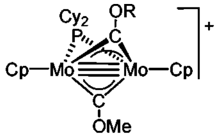
Results and Discussion

Reactions of Complexes 1a,b toward Donor Molecules. As expected for 30-electron species,[1] the complexes **1a**,**b** react readily with simple electron-donor molecules to give the corresponding products derived from the addition of the donors to their unsaturated $\mathrm{Mo_2}$ centers. However, this is accompanied by a C−C coupling between the alkoxycarbyne ligands present in the starting substrate, thus yielding the corresponding alkyne-bridged derivatives.

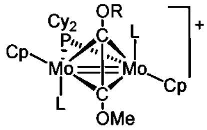
Compound **1a** reacts with CN^{t}Bu (above 243 K) or CO (60 bar, 293 K) to give quantitatively the alkyne-bridged complexes $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\eta^2\text{-}\mathrm{C_2(OMe)_2}\}(\mu\text{-}\mathrm{PCy_2})(\mathrm{L})_2]\mathrm{BF_4}$ [L = CN^{t}Bu (**2**), CO (**3a**)]. In solution, compound **2** is present only as the corresponding *trans* isomer, whereas the dicarbonyl complex **3a** is obtained as a mixture of the isomers *trans*-**3a** and *cis*-**3a** (Chart 1), which in solution are in equilibrium (*trans*-**3a**/*cis*-**3a** = 8 in $\mathrm{CD_2Cl_2}$ at 293 K). In a similar way, compound **1b** reacts under the same conditions with CO to give the new alkyne-bridged complexes $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mathrm{C_2(OEt)(OMe)}\}(\mu\text{-}\mathrm{PCy_2})\text{-}(\mathrm{CO})_2]\mathrm{BF_4}$ (**3b**). This complex also displays *cis*/*trans* isomerism in solution, but here the presence of an asymmetric alkyne ligand renders two possible *cis* isomers, depending on the relative orientation of the alkoxy and carbonyl groups (Chart 1), both of which are present in similar (even if small) amounts (see Experimental Section). The absence of any *cis* isomer for the diisocyanide complex **2** surely is a steric effect, since the almost parallel arrangement of the isocyanide ligands thus implied would lead to severe repulsions between the corresponding ^{t}Bu groups.

As for the bidentate P-donor molecules, we found that compound **1a** does not react with the diphosphine $\mathrm{Ph_2PCH_2PPh_2}$ even in refluxing tetrahydrofuran solutions, perhaps due to unfavorable steric effects. Not surprisingly, the use of a more basic diphosphine such as $\mathrm{Me_2PCH_2PMe_2}$ leads to demethylation of one of the methoxycarbyne ligands, to give almost cleanly the neutral complex $[\mathrm{Mo_2Cp_2}(\mu\text{-}\mathrm{COMe})(\mu\text{-}\mathrm{PCy_2})(\mu\text{-}\mathrm{CO})]$, thus reversing the synthetic route leading to **1a**.[1] However, the reaction of compound **1a** with the diphosphite $\mathrm{(EtO)_2POP(OEt)_2}$ (tedip) proceeds slowly (24 h) to give in quantitative yield the corresponding addition product $[\mathrm{Mo_2Cp_2}\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mathrm{C_2(OMe)_2}\}(\mu\text{-}\mathrm{PCy_2})(\mu\text{-tedip})]\mathrm{BF_4}$ (**4**), in which the P atoms are forced to occupy *cisoid* positions due to the geometrical constraints imposed by the diphosphite backbone.

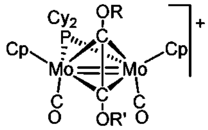
Chart 1



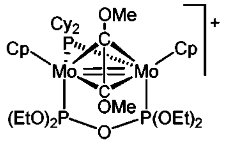
	R
1a	Me
1b	Me



	L	R
2	CN^{t}Bu	Me
trans-**3a**	CO	Me
trans-**3b**	CO	Et



	R	R'
cis-**3a**	Me	Me
cis-**3b**	Me	Et
cis-**3b'**	Et	Me



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Solid-State and Solution Structure of Compound 2. The structure of compound **2** was confirmed through a single-crystal X-ray diffraction study (Figure 1).[2] The molecule displays two MoCp(CN^{t}Bu) fragments in a *transoid* arrangement and bridged by dicyclohexylphosphide and dimethoxyacetylene ligands, so that the P and Mo atoms and the centroid of the C−C bond of the alkyne are all placed roughly in the same plane. The alkyne ligand is slightly twisted (ca. 12°) away from the ideal perpendicular positioning of the C−C bond relative to the intermetallic vector, which results in the presence of two shorter (ca. 2.10 Å) and two longer (ca. 2.27 Å) Mo−C bonds. Although we are not aware of any previous structural determination of a complex containing the unstable dimethoxyacetylene molecule, we note that these lengths only slightly exceed the range of

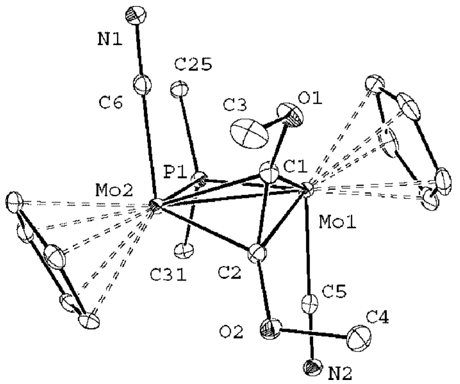

Figure 1. ORTEP diagram (30% probability) of the cation in compound **2**.[2] Cy rings (except the C^1 atoms), ^{t}Bu groups, and H atoms are omitted for clarity.

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(7) (a) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Robert, F. *Organometallics* **2002**, *21*, 11777. (b) Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **1999**, *18*, 634. (c) Alvarez, M. A.; Bois, C.; García, M. E.; Riera, V.; Ruiz, M. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 102.

(8) (a) Nicholas, K. M. *Organometallics* **1982**, *1*, 1713. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 470.

Table 1. Selected IR[a] and NMR[b] Data for New Compounds

compound	ν(CO)	δ(P)	$\delta(\mu\text{-C})/(J_{CP})$
$[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C_2(OMe)_2\}(\mu\text{-}PCy_2)(CN^tBu)_2]BF_4$ (**2**)	2113 (vs)[c], 2063 (w, sh)[c], 1617 (w)[d]	167.0	147.4
$[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C_2(OMe)_2\}(\mu\text{-}PCy_2)(CO)_2]BF_4$ (*trans*-**3a**)	1954 (vs), 1602 (w)[d]	156.7	151.3 (3)
(*cis*-**3a**)	1992 (s)[e]	187.7	
$[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta\text{-}C_2(OEt)(OMe)\}(\mu\text{-}PCy_2)(CO)_2]BF_4$ (*trans*-**3b**)	1953 (vs), 1602 (w)[d]	156.2	150.7 (3), 149.8 (3)
(*cis*-**3b**), (*cis*-**3b′**)	1994 (s)[e]	187.7, 181.1	
$[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}C_2(OMe)_2\}(\mu\text{-}PCy_2)(\mu\text{-tedip})]BF_4$ (**4**)		164.9 (t), 159.7 (d)[f]	158.1 (12, 2), 117.0 (28, 3)
$[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ (**5a**)	1929 (w, sh), 1900 (s), 1652 (w)[g]	128.2[h]	402.8[h]
$[Mo_2Cp_2\{\mu\text{-}C(CO_2Et)\}(\mu\text{-}PCy_2)(CO)_2]$ (**5b**)	1929 (w, sh), 1900 (s), 1652 (w)[g]	128.1[h]	403.3[h]
$[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(\mu\text{-}CO)]$ (**6**)	1702 (s), 1665 (s)[g]	237.1	361.1 (15)
$[Mo_2RuCp_2(\mu\text{-}COMe)_2(\mu\text{-}PCy_2)(CO)_4]BF_4$ (**7**)	2071 (vs), 2026 (s), 1996 (s), 1956 (w)	200.5	385.2 (4), 375.0 (4)

[a] Recorded in dichloromethane solution, ν in cm^{-1}. [b] Recorded in CD_2Cl_2 solutions at 290 K and 121.50 (^{31}P) or 75.48 (^{13}C) MHz, δ in ppm relative to internal TMS (^{13}C) or external 85% aqueous H_3PO_4 (^{31}P); J in Hz. [c] ν(CN). [d] ν (CC). [e] The expected antisymmetric stretch for these isomers is masked by the strong band of the major *trans* isomer. [f] $J_{PP} = 22$. [g] Stretching band of the CO_2R group. [h] Recorded in C_6D_6 solution.

values found for alkyne-bridged compounds of the type $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2R_2)]$ (M = Mo, R = H, Et, Ph;[9a] M = W, R = H)[9b] (M−C lengths in the range 2.22–2.12 Å). In the latter complexes the alkyne ligand is best described as a four-electron donor, displaying C−C bond lengths of ca. 1.33 Å, a figure quite similar to that found for the dimethoxyacetylene ligand in **2** (1.325(3) Å). Thus we can conclude that the bonding situation in compound **2** is similar, although we have to be aware that carbon−carbon distances are not a very reliable probe for analyzing the metal−alkyne bonding.[10] With this caution, we then should formulate a double M−M bond for this 32-electron complex. In agreement with this, the Mo−Mo distance is quite short, 2.6550(5) Å, consistent with a double metal−metal bond in the presence of small donor atoms at the bridging positions. For instance, the intermetallic bond length in the isoelectronic carbyne-bridged complex $[Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(CO)_2]$ is just slightly longer (2.686(1) Å, see below) and that in the azavinylidene complex *trans*-$[Mo_2Cp_2(\mu\text{-}N{=}CHPh)(\mu\text{-}PCy_2)(CO)_2]$ is slightly shorter (2.632(1) Å),[11] with the difference here being mainly attributed to the lower covalent radius of nitrogen, relative to that of carbon.

The spectroscopic data for compound **2** (Table 1 and Experimental Section) are fully consistent with its solid-state structure. In particular, the coupling process leading to the alkyne ligand is clearly denoted by the disappearance of the characteristic highly deshielded ^{13}C NMR resonances of the methoxycarbyne groups (366.0 ppm in **1a**), to render a quite shielded resonance instead (147.4 ppm). The chemical shifts of these C atoms are similar to those previously reported by us for the isoelectronic alkyne-bridged cations $[Mo_2Cp_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}HC_2(p\text{-tol})\}(L)_2(\mu\text{-}L'_2)]^{+2}$ (L = CO, CN^{t}Bu; L′$_2$ = dppm, dmpm);[12] however, we have to point out that all these values are slightly higher than those found for the neutral and electron-precise complexes $[M_2Cp_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}C_2R_2)]$ mentioned above.[9] This possibly reflects not only the higher charge and oxidation state of the molybdenum atoms in our complexes, but also the difference in the total electron count for these molecules (32-electron vs 34-electron species). On the other hand, the ^{31}P NMR spectrum of **2** displays a relatively deshielded resonance (167.0 ppm) when compared to other related 32-electron complexes such as $[Mo_2Cp_2(\mu\text{-}\eta^1{:}\eta^2\text{-}CMe{=}CH_2)(\mu\text{-}PCy_2)(CO)_2]$ (131.2 ppm).[13] This might possibly be attributed to a less efficient donor ability of the dimethoxyacetylene bridge in the cationic complex, when compared with that of an alkenyl ligand, since such electronic property seems to correlate with the ^{31}P chemical shifts in molecules of the type *trans*-$[Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}X)(CO)_2]$.[14] We finally note that the IR spectrum of **2** shows, in addition to the main C−N stretching band at 2113 cm^{-1}, a weak additional C−N band at 2063 cm^{-1}. This is not unusual for terminal isocyanide ligands, which can adopt slightly bent conformations in solution, along with the more stable (linear) conformations.[15]

Solution Structure of the Dicarbonyls 3a,b. As stated above, these complexes are obtained as a mixture of isomers differing in the relative positioning of the MoCp(CO) fragments, with the isomer *trans* being dominant in both cases.

For compound **3a** two sharp resonances are present in its ^{31}P NMR spectrum. The resonance for the major isomer (*trans*-**3a**) is only slightly more shielded than that of the *trans*-diisocyanide analogue **2** (156.7 vs 167.0 ppm), while the minor isomer (*cis*-**3a**) exhibits a resonance some 30 ppm more deshielded (187.7 ppm). This seems to be a spectroscopic feature of the *cis*/*trans* isomerism in these 32-electron complexes, and it has been previously detected in the isoelectronic bis(phosphide) pairs *cis*- and *trans*-$[Mo_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}PR'_2)(CO)_2]$ (R = R′ = Ph; R = Ph, R′ = ^{t}Bu), with the resonances corresponding to the *cis* isomers appearing some 45 ppm above those of the *trans* isomers.[16] The IR spectrum also reflects the presence of two isomers: for the major isomer (*trans*-**3a**) we can clearly identify one strong band in the region of terminal carbonyls (1954 cm^{-1}), consistent with the presence of two CO ligands arranged *trans*, almost antiparallel to each other;[17] in addition, there is a weak band at higher frequencies (1992 cm^{-1}), which can be assigned to the symmetric C−O stretch of its *cis*-dicarbonyl isomer *cis*-**3a**. Similar trends in the C−O stretching frequencies have been found for the *cis* and *trans* isomers of the mentioned bis(phosphide) complexes.[16] The existence of a C_2 symmetry axis in the major isomer *trans*-**3a** is clearly denoted by the simplicity of the ^1H and ^{13}C NMR spectra, displaying single resonances for the pairs of equivalent Cp, OMe, and CO

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(9) (a) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764. (b) Ginley, D. S.; Bock, C. R.; Wrighton, M. S.; Fischer, B. E.; Tipton, D. L.; Bau, R. *J. Organomet. Chem.* **1978**, *157*, 41.

(10) (a) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1. (b) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.

(11) Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A. *Organometallics* **2007**, *26*, 1461.

(12) Alvarez, M. A.; Anaya, Y.; García, M. E.; Ruiz, M. A. *J. Organomet. Chem.* **2007**, *692*, 983.

(13) García, M. E.; Melón, S.; Ramos, A.; Riera, V.; Ruiz, M. A.; Belletti, D.; Graiff, C.; Tiripicchio, A. *Organometallics* **2003**, *22*, 1983.

(14) García; , M. E.; Ramos, A.; Ruiz, M. A.; Lanfranchi, M.; Marchio, L. *Organometallics* **2007**, *26*, 6197.

(15) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

(16) (a) García, M. E.; Riera, V.; Ruiz, M. A.; Rueda, M. T.; Sáez, D. *Organometallics* **2002**, *21*, 5515. (b) Alvarez, M. A.; García, M. E.; Martinez, M. E.; Ramos, A.; Ruiz, M. A.; Sáez, D.; Vaissermann, J. *Inorg. Chem.* **2006**, *45*, 6965.

(17) Braterman, P. S. *Metal Carbonyl*; Academic Press: London, 1975.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 4

Mo(1b)−Mo(2b)	2.655(1)	Mo(1b)−Mo(2b)−P(3b)	94.6(1)
Mo(1b)−C(1b)	2.131(7)	Mo(2b)−Mo(1b)−P(2b)	90.1(1)
Mo(2b)−C(1b)	2.207(6)	Mo(1b)−C(1b)−Mo(2b)	75.5(2)
Mo(1b)−C(2b)	2.273(7)	Mo(1b)−C(2b)−Mo(2b)	73.4(2)
Mo(2b)−C(2b)	2.166(6)	Mo(1b)−P(1b)−Mo(2b)	67.3(1)
Mo(1b)−P(1b)	2.401(2)	P(1b)−Mo(1b)−P(2b)	93.3(1)
Mo(2b)−P(1b)	2.394(2)	P(1b)−Mo(2b)−P(3b)	93.5(1)
Mo(1b)−P(2b)	2.390(2)	C(1b)−Mo(1b)−P(2b)	111.7(2)
Mo(2b)−P(3b)	2.373(2)	C(1b)−Mo(2b)−P(3b)	115.9(2)
C(1b)−C(2b)	1.345(9)	C(2b)−Mo(1b)−P(2b)	76.3(2)
C(1b)−O(1b)	1.369(7)	C(2b)−Mo(2b)−P(3b)	80.4(2)
O(1b)−C(3b)	1.428(8)	C(1b)−O(1b)−C(3b)	114.6(5)
C(2b)−O(2b)	1.356(8)	C(2b)−O(2b)−C(4b)	113.6(5)
O(2b)−C(4b)	1.417(10)	P(2b)−O(5b)−P(3b)	121.9(3)

groups, as well as six ^{13}C resonances for the equivalent cyclohexyl groups. Due to its low relative proportion, not all resonances of the isomer *cis*-**3a** could be identified in these spectra, but the data available are informative enough to support the proposed structure. In particular, the ^{1}H and ^{13}C spectra exhibit one Cp but two OMe resonances, in agreement with the presence of a symmetry plane, rather than a C_2 axis, relating the metal fragments of the molecule.

The spectroscopic data for the ethoxy(methoxy)acetylene complex **3b** (Table 1 and Experimental Section) are very similar to those just discussed for the complex **3a**, and then a detailed analysis is not needed, although there are some minor differences. First, its IR spectrum lacks a high-frequency band, indicative of the inexistence or very low proportion of any *cis* isomers. In agreement with this, the ^{31}P NMR spectrum reveals the presence of two very minor resonances in the region expected for these *cis*-dicarbonyls (ca. 187 ppm), along with the resonance of the major *trans* isomer (156.2 ppm). The asymmetry of the alkyne ligand implies for the major isomer *trans*-**3b** the absence of any symmetry elements, this explaining the appearance of independent resonances for each of the Cp and CO groups and the appearance of 12 ^{13}C cyclohexyl resonances. In contrast, both *cis* isomers (differing in the relative orientation of the alkoxy groups with respect to the CO ligands, Chart 1) display equivalent cyclopentadienyl ligands.

Solid-State and Solution Structure of Compound 4. The structure of compound **4** was confirmed through a single-crystal X-ray diffraction study (Table 2 and Figure 2). The asymmetric unit contains two independent molecules of the complex with no major differences between them. As it can be seen, the cation in **4** displays two *cisoid* MoCp moieties bridged by three ligands, dimethoxyacetylene, diphosphite, and dicyclohexylphosphide, with the Mo and P atoms, and the centroid of the C−C bond of the alkyne placed almost in the same plane, while the diphosphite ligand is placed perpendicular to that plane (P−Mo−P angles ca. 94°). The intermetallic distance, 2.655(1) Å, is identical to that found for the diisocyanide complex **2** and, therefore, consistent with the double metal−metal bond formulated according to the EAN rule. The *cisoid* arrangement of MoCp moieties in **4** has little effect (compared to **2**) on the Mo−C and C−C bond lengths of the alkyne either, although the alkyne ligand is now placed almost perfectly perpendicular to the metal−metal bond (twist angle of ca. 4°), probably as a consequence of the steric pressure induced by the proximity of the ethoxy groups of the tedip ligand. We note also that both the phosphide and diphosphite ligands display similar M−P bond lengths, a feature previously found by us for related compounds such as the electron-precise hydride [$Mo_2Cp_2(\mu$-H)(μ-PCy_2)$(CO)_2$(μ-tedip)].[11]

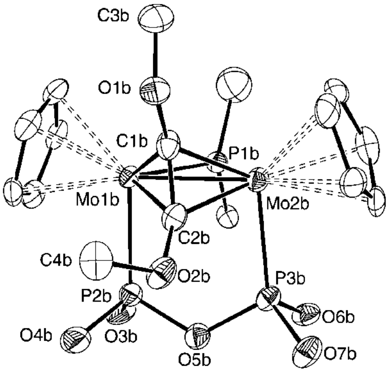

Figure 2. ORTEP diagram (30% probability) of the cation in compound **4**. Cy rings (except the C^1 atoms), ^{t}Bu and Et groups, and H atoms are omitted for clarity. Only one of the two independent molecules present in the asymmetric unit is shown.

Spectroscopic data in solution for compound **4** are fully consistent with the structure found in the crystal. The ^{31}P NMR spectrum displays a doublet at 159.7 ppm, in the same region as other tedip-bridged dimolybdenum complexes,[11,18] and a triplet at 164.9 ppm, which is therefore assigned to the phosphide ligand, with a chemical shift similar to that in **2**. The coupling between phosphite and phosphide P atoms (J_{PP} = 22 Hz) falls in the lower part of the range usually found for a *cis* arrangement in this type of cyclopentadienyl complexes.[19] On the other hand, the presence of a symmetry plane (rather than a C_2 symmetry axis) relating both metal centers in **4** causes the appearance in the corresponding ^{1}H and ^{13}C NMR spectra of just one resonance for the equivalent Cp ligands, but two separated ones for the methoxyl groups of the bridging alkyne. The metal-bound C atoms also give rise to separated resonances (δ_C = 158.1 ppm, triplet of doublets(td) with J_{CP} = 12, 2 Hz; δ_C = 117.0 ppm, td with J_{CP} = 28, 3 Hz). By considering the general trends for $^{2}J_{XY}$ in complexes of the type $CpMXYL_2$,[20,21] we can justify that the lower couplings (with values of 2 and 3 Hz, respectively) correspond to those with the phosphide ligand, since the corresponding C−Mo−P angles are all similar (ca. 103° for C(1b) and 108° for C(2b), Figure 2). In addition, the values of the tedip-alkyne P−C couplings allow us to assign the more strongly coupled resonance (117 ppm) to that of the carbon atom placed closer to the tedip bridge (C(2b) in Figure 2), since this implies the smaller P−Mo−C angle (ca. 78° in the crystal). In contrast, the carbon atom closer to the Cp ligands (C(1b) in Figure 2) displays much larger C−Mo−P angles (ca. 113° in the crystal), and therefore it is expected to display a smaller P−C coupling, as found for the 158.1 ppm resonance (J_{CP} = 12 Hz). Note the large chemical shift difference (δ = 41.1 ppm) between these two carbon resonances, derived just from their different positioning with respect to the tedip ligand, an effect perhaps related to their distinct average Mo−C bond lengths [2.17 Å for C(1b) and 2.22 Å for C(2b)].

Reversibility of the Carbyne−Carbyne Coupling. The C−C bond formation process leading to the dimethoxyacetylene complexes **2** to **4** was found to be fully reversible in the case

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[18] Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics* **1992**, *11*, 2854.

[19] Alvarez, M. A.; Anaya, Y.; García, M. E.; Riera, V.; Ruiz, M. A. *Organometallics* **2004**, *23*, 433.

[20] Jameson, C. H. In *Phosphorous-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: New York, 1987; Chapter 6.

[21] Wrackmeyer, B.; Alt, H. G.; Maisel, H. E. *J. Organomet. Chem.* **1990**, *399*, 125.

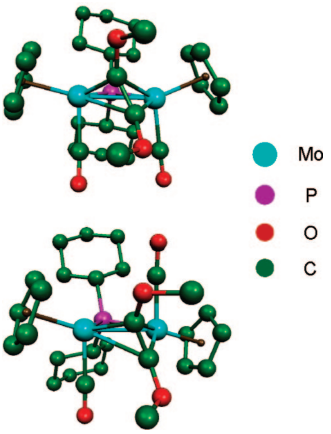


Figure 3. Optimized geometries for complexes *cis*-**3a** and *trans*-**3a**, with hydrogen atoms omitted for clarity.

of the dicarbonyl products **3a**,**b**. In fact, the latter experience easily the loss of both CO ligands under visible−UV irradiation in THF solutions, to regenerate rapidly (ca. 5 min) and quantitatively (by NMR) the corresponding parent bis(alkoxycarbyne) complexes **1a**,**b**. No intermediates were detected in this double-decarbonylation process. As stated above, only two precedents for a reversible coupling between carbyne ligands have been reported previously,[5,6] and the closest precedent involving binuclear complexes is the irreversible cleavage of alkynes induced by triply bonded ditungsten alkoxide or silyloxide complexes.[22]

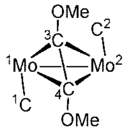
In contrast to the above results, neither of the complexes **2** or **4** undergoes a related transformation under thermal or photochemical activation. Since the geometric parameters calculated for the dicarbonyls *cis*- and *trans*-**3a** show no special weakness in the C−C bond of the dimethoxyacetylene ligand (see below), then we have to conclude that the reversibility of the C−C coupling reaction involved in the **1**/**3** transformation is due to no special labilization effect on that C−C bond, but just to the experimental facilities to add and remove CO molecules from the dimetal center in these complexes.

DFT Calculations on the Dicarbonyl Compounds 3a. The great computational efficiency and chemical accuracy of the DFT methods currently under use allows carrying out quantum mechanical studies of real (rather than model) systems of the size of the binuclear compounds here discussed.[23] We have thus carried out DFT calculations on both isomers of compound **3a** (*cis* and *trans*, see Experimental Section for further details), to gain a better understanding of the bonding and easy C−C bond cleavage in these cations.

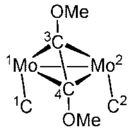
Table 3. Selected Data of the DFT-Optimized Structures of Compounds *cis*-3a and *trans*-3a[a]

parameter	*trans*-**3a**	*cis*-**3a**
Mo(1)−Mo(2)	2.750	2.759
Mo(1)−C(1)	1.988	1.995
Mo(2)−C(2)	1.985	2.014
Mo(1)−C(3)	2.108	2.086
Mo(1)−C(4)	2.475	2.527
Mo(2)−C(3)	2.473	2.397
Mo(2)−C(4)	2.108	2.102
Mo(1)−P	2.450	2.446
Mo(2)−P	2.450	2.446
C(3)−C(4)	1.358	1.368
C(3)−OMe	1.338	1.349
C(4)−OMe	1.338	1.329
C(1)−Mo(1)−Mo(2)	84.7	87.5
C(2)−Mo(2)−Mo(1)	85.9	99.4
Mo(1)−P−Mo(2)	68.3	68.7

[a] Bond lengths and angles in Å and deg, respectively, according to the labeling shown in the figure below.

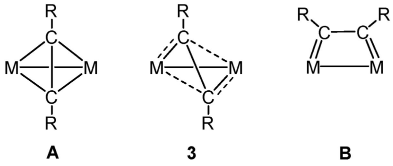


trans-**3a**



cis-**3a**

Chart 2



The most relevant parameters derived from the geometry optimization of these cations (Figure 3) can be found in Table 3. The optimized geometries for both isomers exhibit similar bond lengths, so it can be concluded that the relative arrangement of the MoCp(CO) moieties has little effect on the bonding within the central core of the molecule. The intermetallic distances found in both isomers (ca. 2.755 Å) are somewhat longer than those experimentally determined for the complexes **2** and **4** (ca. 2.66 Å). Although we,[1] and others,[23] have found previously that the B3LYP-optimized bond distances involving transition metal atoms tend to be slightly longer than those determined crystallographically, the difference found here (ca. 0.1 Å) is noticeably higher. Thus, we conclude that the intermetallic length in the dicarbonyls **2a** surely is genuinely higher than those in the complexes **2** and **4**. It is thus tempting to associate this weakening of the intermetallic interaction to the better π-acceptor properties of the carbonyl ligands (when compared to those of the CN^{t}Bu or tedip groups), which implies a lower electron density at the metal centers. We also note that the molecular orbitals (MOs) calculated for both *cis*-**3a** and *trans*-**3a** are in good agreement with the double M−M bond proposed for these cations on the basis of the EAN rules, since the expected σ_{MM} and π_{MM} bonding MOs can be found in both cases (see Supporting Information).

A relevant feature in the structure of these isomers is the strong twist angle of the alkyne ligand with respect to the perpendicular of the intermetallic vector (26−28°, to be compared with 4° and 12° for compounds **4** and **2**, respectively). This causes large differences (ca. 0.4 Å) in the Mo−C bond lengths involving the alkyne, with the short distances (ca. 2.10 Å) approaching the values calculated for the Mo−carbyne bonds in **1a** (ca. 2.02 Å)[1] and the long distances (ca. 2.50 Å) being much longer than expected for single Mo−C bonds. In contrast, the C−C bond displays a normal length of ca. 1.36 Å. All this suggests a significant distortion in the coordination mode of the alkyne, away from the perpendicular mode, toward the parallel bis-carbene mode, which also implies a four-electron contribution to the dimetal center (**A** and **B** in Chart 2). Indeed, the environment around the Mo-bound alkyne atoms is close to trigonal rather than tetrahedral (sum of angles around these

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(22) (a) Chamberlain, R. M. L.; Rosenfeld, D. C.; Wolczanski, P. T.; Lobkovsky, E. B. *Organometallics* **2002**, *21*, 2724. (b) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74.

(23) (a) Koch, W.; Holthausen, M. C. A. *Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, 2002. (b) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651. (c) Foresman, J. B., Frisch, A. E. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, 1996.

Table 4. Topological Properties of the Electron Density at the Bond Critical Points[a]

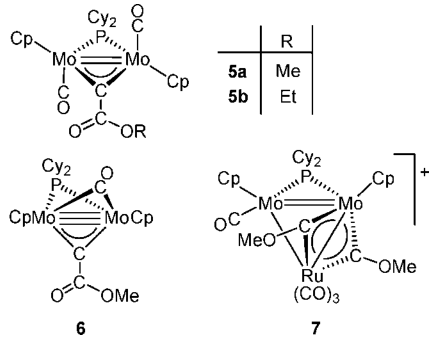
	cis-**3a**		*trans*-**3a**	
bond	ρ	$\nabla^2\rho$	ρ	$\nabla^2\rho$
Mo(1)−Mo(2)	0.397	0.869	0.403	0.933
Mo(1)−C(1)	0.849	9.554	0.867	9.760
Mo(2)−C(2)	0.810	9.570	0.860	9.767
Mo(1)−C(3)	0.790	5.089	0.760	4.728
Mo(2)−C(4)	0.750	5.706	0.760	4.721
C(3)−C(4)	2.178	−20.836	2.242	−22.301
C(3)−OMe	1.968	−5.060	2.024	−4.895
C(4)−OMe	2.052	−3.223	2.026	−4.825

[a] Labeling scheme according to the figure in Table 3. Values of the electron density (ρ) and its Laplacian ($\nabla^2\rho$) at these points are given in e Å^{-3} and e Å^{-5}, respectively.

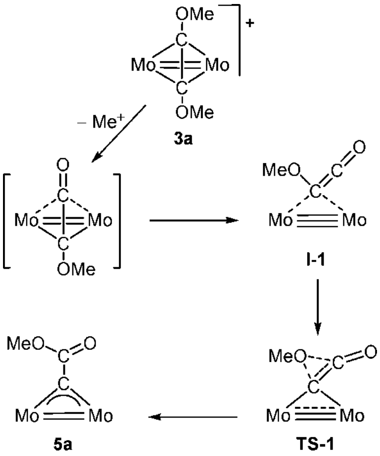
atoms being ca. 359° for *cis*-**3a** and 358° for *trans*-**3a**). We feel that further studies, these including different alkyne ligands, are needed to conclude whether the strong twist of the alkyne bridge in these dicarbonyl cations has an electronic or steric origin (or a combination of both), and experimental work in that direction is being undertaken in our laboratory.

To obtain complementary information on the coordination of the alkyne in the dicarbonyls **3a**, we have also carried out a topological analysis of the electron density on these systems by means of the quantum theory of atoms in molecules (AIM),[24] with the resulting values of the electron density (ρ) and its Laplacian ($\nabla^2\rho$) at several bond critical points (bcp) of both *cis*- and *trans*-**3a** being collected in Table 4. The first point of interest is the location of the corresponding M−M bcp, a feature not granted for metal−metal bonded complexes having bridging ligands.[25] The values of the electron density at these bcp's (ca. 0.40 e Å^{-3}) are similar to those recently computed by us for other molecules with formal metal−metal double bonds such as the methoxycarbyne complex [$Mo_2Cp_2(\mu$-COMe)(μ-$PCy_2)(CO)_2$] (0.42 e Å^{-3}).[26] As for the Mo_2C_2 tetrahedron, only the bcp's corresponding to the shorter Mo−C bonds are located. The corresponding electron densities (0.76–0.79 e Å^{-3}) are intermediate between the values computed for the Mo−C single bonds of bridging carbonyls (ca. 0.71 e Å^{-3}) and the Mo−C multiple bonds of bridging methoxycarbynes (formal bond order 1.5; 0.83–0.93 e Å^{-3}),[1,26] and thus suggest the presence of substantial multiplicity in these bonds, which is in agreement with the trigonal environment of the C atoms and with an incipient carbene-like character of these Mo−C bonds (Chart 2). Finally, the values of the electron density at the C−C bcp of the alkyne ligand (ca. 2.21 e Å^{-3}) are lower than those computed for free alkynes (2.44–2.56 e Å^{-3}),[27] in agreement with the expected decrease of the electron density upon coordination,[10a] but we have no data on coordinated alkynes to be used for comparative purposes. We note, however, that the calculated densities at the alkyne C−C bcp's in *cis*-**3a** and *trans*-**3a** are yet considerably higher than that computed for the C(sp^2)−C(sp^2) single bond in [$Mo_2Cp_2\{\mu$-$C(CO_2Me)\}(\mu$-$PCy_2)(CO)_2$] (1.93 e Å^{-3}).[26]

Chart 3



Scheme 1. Proposed Reaction Pathway for the Formation of Compound 5a [Mo = MoCp(CO); the bridging PCy_2 ligand is omitted for clarity]



Reaction of the Alkyne-Bridged Complexes 3a,b with DBU. As stated above, the formation and cleavage of the C−C bond in the cluster [$Fe_4(\eta^5$-$C_5H_4Me)_4(\mu$-$CH)_2(\mu_3$-$CO)_3$] can be triggered by two-electron redox processes.[6] We thus decided to check whether redox reactions could be used to modify the C−C bonding of the alkyne ligand in the cations **2** to **4**. Unfortunately, these complexes turned to be quite resistant to oxidation, surely due to the positive charge already present in these molecules. As for the reduction reactions, we found that complexes **2** and **3a**,**b** react readily with strong reducing agents such as Na(Hg) or sodium naphthalenide, but complex mixtures were obtained in both cases. Demethylation of the coordinated alkyne was suspected to be one of the undergoing processes. Indeed, when the dicarbonyl complex **3a** is treated with the strong base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), demethylation of the bonded alkyne is cleanly accomplished, but gives unexpectedly the neutral complex [$Mo_2Cp_2\{\mu$-$C(CO_2Me)\}(\mu$-$PCy_2)(CO)_2$] (**5a**) (Chart 3), bearing a 2-methoxy-2-oxoethylidyne bridging ligand (also referred to as carboxycarbyne). This seems to be the result of a 1,2-shift of the methoxyl group remaining in the ketenyl intermediate (not detected), which is presumably formed after the initial demethylation in **3a** (Scheme 1, see below). However, the treatment of the ethoxy(methoxy) acetylene complex **3b** with DBU has a poor selectivity, and both demethylation and deethylation occur in similar proportions, to give a roughly equimolar mixture of the complexes **5a** and its ethoxyl-substituted analogue [$Mo_2Cp_2\{\mu$-$C(CO_2Et)\}(\mu$-$PCy_2)(CO)_2$] (**5b**). Unfortunately, these very similar compounds could not be fully separated by either chromatography or crystallization, and therefore the data for compound **5b** had to be extracted from the spectroscopic analysis of these mixtures.

Solid-State and Solution Structure of Compounds 5a,b. The structure of compound **5a** was confirmed through a single-crystal X-ray diffraction study (Table 5 and Figure 4). The

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[24] (a) Bader, R. F. W. *Atoms in Molecules-A Quantum Theory*; Oxford University Press: Oxford, 1990. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893.

[25] Macchi, P.; Sironi, A. *Coord. Chem. Rev.* **2003**, *383*, 238–239.

[26] García, M. E.; García-Vivó, D.; Ruiz, M. A.; Aullón, G.; Alvarez, S. *Organometallics* **2007**, *26*, 5912.

[27] Grabowski, S. J.; Krygowski, T. M. *Chem. Phys. Lett.* **2004**, *389*, 51.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 5a

Mo(1)−Mo(2)	2.656(1)	Mo(1)−Mo(2)−C(5)	82.7(2)
Mo(1)−C(1)	1.993(5)	Mo(2)−Mo(1)−C(4)	85.5(3)
Mo(2)−C(1)	1.977(6)	Mo(1)−C(1)−Mo(2)	84.0(2)
Mo(1)−C(4)	1.993(8)	Mo(1)−P−Mo(2)	67.2(1)
Mo(2)−C(5)	2.015(7)	Mo(1)−C(1)−C(2)	139.8(4)
Mo(1)−P	2.409(2)	Mo(2)−C(1)−C(2)	135.5(4)
Mo(2)−P	2.394(2)	C(1)−C(2)−O(2)	124.7(5)
C(1)−C(2)	1.447(8)	O(2)−C(2)−O(3)	122.3(5)
C(2)−O(2)	1.215(7)	C(1)−C(2)−O(3)	113.1(5)
C(2)−O(3)	1.353(7)	C(4)−Mo(1)−P	84.0(3)
O(3)−C(3)	1.448(7)	C(5)−Mo(2)−P	85.3(2)

molecule displays two MoCp(CO) fragments in a *transoid* arrangement bridged by dicyclohexylphosphide and carboxycarbyne ligands, with the latter group twisted ca. 29° from the perpendicular to the intermetallic vector and the carbonyl ligands slightly bent over that vector (C−Mo−Mo ca. 84°). The latter is a characteristic feature of electron-deficient molecules of the type [$Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}X)(CO)_2$] (X = one- to three-electron donor group).[11,14] The Mo−Mo separation is quite short, 2.656(1) Å, consistent with a double metal−metal bond in the presence of a bridging atom of small covalent radius, as discussed above (see discussion of the structures of complexes **2** and **4**). On the other hand, the Mo−C(carbyne) distances (ca. 1.98 Å) are almost identical to those previously measured for alkoxycarbyne complexes such as **1a**[1] or [$Mo_2Cp_2(\mu\text{-}COEt)(\mu\text{-}PCy_2)(\mu\text{-}CO)$],[13] an observation that in turn is consistent with our recent calculations pointing to a substantial similarity between these two types of carbyne ligands.[26] Finally, we note that the twisted conformation of the CO_2Me group with respect to the intermetallic vector rules out the possibility of a π interaction with the carbyne C atom. Accordingly, the bonding distances within this fragment are similar to those found in organic molecules. For instance, the C(1)−C(2) bond length of 1.447(8) Å is fully consistent with the presence of a single C−C bond between these sp^2-hybridized atoms.[28]

The spectroscopic data in solution for compound **5a** (Table 1 and Experimental Section) are fully consistent with its solid-state structure, and those for the ethoxyl compound **5b** are almost identical and therefore need no specific comments. The carbonyl ligands in these complexes give rise to two C−O stretching bands with the typical pattern of *trans*-dicarbonyl complexes (weak and strong, in order of decreasing frequency) defining angles between CO groups close to 180°.[17] We note, however, that the average C−O stretching frequencies (1915 cm^{-1}) are substantially higher than that figure in the isostructural methoxycarbyne complex [$Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_2$] (1878 cm^{-1}).[26] This suggests a considerable electron-acceptor character of the carboxycarbyne ligand, as far as the metal centers are concerned. On the other hand, the ^{31}P NMR spectrum of **5a** exhibits a resonance at 128.2 ppm that falls in the range found for related 32-electron compounds of the type *trans*-[$Mo_2Cp_2(\mu\text{-}PCy_2)(\mu\text{-}X)(CO)_2$] (X = 3e-donor ligand),[13,14,16] while the presence of the bridging carbyne is denoted by the appearance of a strongly deshielded resonance in the ^{13}C NMR spectrum (402.8 ppm), with a shift similar to that of the isoelectronic methoxycarbyne complex [$Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_2$] (404.0 ppm).[26] As expected, the ^{13}C NMR spectrum of **5a** displays just one resonance for the CO and Cp ligands, in agreement with the presence of a C_2 symmetry axis (by assuming free rotation of the CO_2Me around the single C−C bond) and a six-resonances pattern for the equivalent cyclohexyl rings.

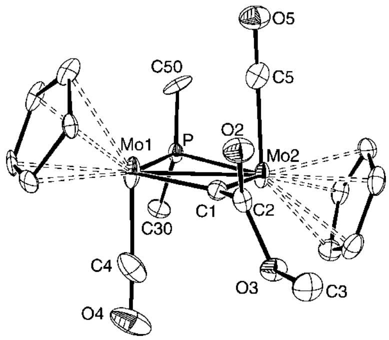

Figure 4. ORTEP diagram (30% probability) of compound **5a**. Cy rings (except the C^1 atoms) and H atoms are omitted for clarity.

Decarbonylation of Compound 5a. The methoxycarbyne complex [$Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(CO)_2$] undergoes photochemical decarbonylation to give the triply bonded complex [$Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)$].[26] It was thus expected that the carboxycarbyne complex **5a** might exhibit a similar behavior. Indeed, the photolysis of toluene solutions of **5a** with visible−UV light gives with good yield the monocarbonyl derivative [$Mo_2Cp_2\{\mu\text{-}C(CO_2Me)\}(\mu\text{-}PCy_2)(\mu\text{-}CO)$] (**6**) (Chart 3).

Spectroscopic data for compound **6** (Table 1 and Experimental Section) are similar to those of the related alkoxycarbyne complexes [$Mo_2Cp_2(\mu\text{-}COR)(\mu\text{-}PCy_2)(\mu\text{-}CO)$] (R = Me, Et)[13] and firmly support the geometry proposed, made up of two MoCp moieties bridged by CO, carboxycarbyne, and dicyclohexylphosphide ligands (Chart 3). The bridging carbonyl gives rise to a low-frequency C−O stretching band (1665 cm^{-1}) and to a characteristic strongly deshielded ^{13}C NMR resonance (299.5 ppm), to be compared with the values of 1674 cm^{-1} and 305.0 ppm for the carbonyl ligand in [$Mo_2Cp_2(\mu\text{-}COMe)(\mu\text{-}PCy_2)(\mu\text{-}CO)$].[13] As expected, the bridgehead C(carbyne) atom displays an even more deshielded ^{13}C NMR resonance (361.1 ppm, to be compared with a value of 352.0 ppm for the mentioned methoxycarbyne complex). Finally, the presence of only one resonance for the Cp ligands in the ^1H and ^{13}C NMR spectra, and the appearance of eight ^{13}C resonances for the inequivalent cyclohexyl rings, gives further support to the overall symmetry proposed for this molecule.

DFT Study of the 1,2-Methoxyl Shift Leading to the Carbyne Complex 5a. DFT methods currently under use have proved to be useful for the prediction of geometries and energies not only of ground states but also of the transition states of metal complexes.[29] In the case of the reaction transforming the dimethoxyacetylene complex **3a** into the carboxycarbyne **5a** we could detect no intermediates by IR or NMR monitoring of the reaction mixture. Yet we can rationalize the results by assuming that a demethylation of the dimethoxyacetylene ligand of **3a** would occur first, to initially generate a $\mu\text{-}\eta^2{:}\eta^2$-bonded ketenyl ligand (Scheme 1), which was taken as the starting point of our calculations. The latter show that this structure is unstable with respect to its $\mu\text{-}\eta^1{:}\eta^1$-ketenyl isomer (**I-1**), so we suppose that this change in the coordination mode of the ketenyl ligand occurs very rapidly. The undetected intermediate **I-1** is calculated to undergo a 1,2-shift of the OMe group through the

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(28) (a) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity,* 4th ed.; HarperCollins College Publications: New York, 1993. (b) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(29) (a) Ziegler, T.; Autschbach, J. *Chem. Rev.* **2005**, *105*, 2695. (b) Niu, S.; Hall, M. B. **2000**, *100*, 353.

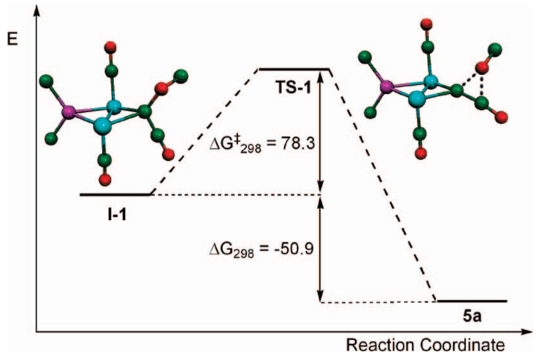
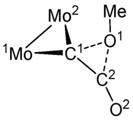


Figure 5. Energy profile (kJ/mol) for the 1,2-shift of the OMe group leading to compound **5a**, showing the DFT-optimized structures for **I-1** and **TS-1** (see text), with Cy rings (except the C^1 atoms) and Cp ligands omitted for clarity.

Table 6. Selected Data of the DFT-Optimized Structures of Complexes I-1, TS-1, and 5a[a]

parameter	I-1	TS-1	5a[b]
Mo(1)−Mo(2)	2.630	2.657	2.699
Mo(1)−C(1)	2.236	2.116	2.000
Mo(2)−C(1)	2.202	2.120	2.006
Mo(1)−CO	1.968	1.963	1.981
Mo(2)−CO	1.953	1.958	1.978
C(1)−C(2)	1.351	1.353	1.455
C(1)−O(1)	1.412	1.775	2.441
C(2)−O(1)	2.377	1.797	1.364
C(2)−O(2)	1.175	1.173	1.220
O(1)−Me	1.422	1.424	1.430
Mo(1)−P	2.447	2.452	2.454
Mo(2)−P	2.451	2.450	2.460
O(1)−C(1)−C(2)	118.6	68.9	118.5
C(1)−C(2)−O(2)	177.0	168.5	121.6

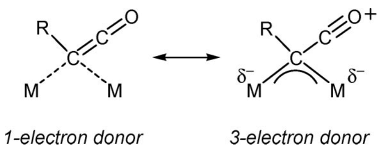
[a] Bond lengths (Å) and angles (deg) according to the labeling shown in the figure (see text). [b] Data taken from ref 26.



transition state **TS-1** to finally give the carboxycarbyne compound **5a**. We note that the DFT-optimized geometry and electronic structure of **5a** was reported recently by us in the context of an analysis of the metal−alkoxycarbyne bonding.[26]

Figure 5 shows a diagram of the reaction profile for the **I-1**/**5a** transformation including the views of the optimized geometries for **I-1** and **TS-1**. The most relevant parameters derived from the geometry optimization of these structures can be found in Table 6. As for the ketenyl complex **I-1**, its intermetallic distance (2.630 Å) is intermediate between those computed for the doubly bonded carbyne **5a** (2.699 Å)[26] and for the triply bonded hydride $[Mo_2Cp_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_2]$ (2.535 Å),[14] and therefore suggests that the ketenyl ligand in this intermediate is effectively providing the dimetal center with more than one electron. This effect has been previously found in other ketenyl complexes, such as the heterometallic complex $[FeWCp\{\mu\text{-}C(SiPh_3)CO\}(CO)_5]$, and can be rationalized by assuming the contribution of ketenyl (one-electron donor) and acylium (three-electron donor) resonant forms to the electronic structure of the bridging ligand (Chart 4).[30] Accordingly, the Mo−C bond distances in **I-1** (ca. 2.22 Å) are significantly shorter than those computed for the phenyl complex $[Mo_2Cp_2(\mu\text{-}Ph)(\mu\text{-}PCy_2)(CO)_2]$ (2.333 Å),[14] taken here as a rough model for a one-electron C-donor ligand, while the C−C length (1.35 Å) is somewhat higher than that expected for a C(sp^2)−C(sp) double bond (ca. 1.31 Å).[28]

Chart 4



In the transition state **TS-1** the Mo−C distances become shorter, reflecting the progressive transformation of the hydrocarbyl bridge into a carbyne ligand, which displays even shorter Mo−C bond distances (2.00 Å), then corresponding to a formal Mo−C bond order of 1.5. As expected, the methoxyl group is located in the middle of the way from one carbon to the other, and the corresponding C−O(1) lengths are comparable to each other (ca. 1.78 Å) and both of them are longer than the reference single C−O bond lengths (ca. 1.4 Å). The computed activation barrier corresponding to this movement is modest ($\Delta G^{\ddagger}_{298}$ = 78 kJ mol^{-1}), and the overall process from **I-1** to **5a** is thermodynamically favorable, as expected (ΔG_{298} =78 kJ mol^{-1}). We should note that, to the best of our knowledge, no ketenyl complex having an alkoxyl substituent seems to have been ever detected, a circumstance perhaps related to the facile migration of this group between adjacent carbon atoms here analyzed. This behavior might be specific of alkoxyl substituents, as opposed to alkyl or aryl groups. In fact, we have recently prepared in our laboratory an isoelectronic phenylketenyl analogue of complex **I-1**, $[Mo_2Cp_2\{\mu\text{-}\eta^1{:}\eta^1\text{-}C(CO)Ph\}(\mu\text{-}PCy_2)(CO)_2]$, a molecule with a structure comparable to that of **I-1**, according to an X-ray diffraction study, but thermally stable, with no tendency for aryl migration.[31]

Reaction of Compound 1a with $[Ru_3(CO)_{12}]$. In the previous sections we have shown that the reaction of compound **1a** with different donor molecules induces C−C coupling between the methoxycarbyne ligands there present. We then decided to check whether the incorporation of 16-electron metal fragments of the type $M(CO)_x$ or $MCp(CO)_x$, isolobally related to the methylene fragment, might also induce related coupling reactions. Unfortunately, perhaps due to its cationic nature, complex **1a** has a very low basicity and does not react with most of the classical precursors of 16-electron metal fragments such as $[MnCp'(THF)(CO)_2]$ (Cp′ = C_5H_4Me), $[Fe_2(CO)_9]$, or $[Mo(CO)_6]$ under either thermal or photochemical activation. However, reaction with $[Ru_3(CO)_{12}]$ does occur under visible−UV light irradiation to give almost quantitatively the new 46-electron trinuclear cluster $[Mo_2RuCp_2(\mu\text{-}COMe)_2(\mu\text{-}PCy_2)(CO)_4]BF_4$ (**7**) (Chart 3). Indeed the formation of this cluster is accompanied by a rearrangement of the methoxycarbyne ligands, but no C−C coupling is induced in the process.

The structure of compound **7** was confirmed through a single-crystal X-ray diffraction study (Figure 6 and Table 7). The cation can be viewed as the result of the addition of a $Ru(CO)_4$ fragment to the unsaturated dimetal center of **1a**, followed by a reorganization of the carbyne and carbonyl ligands so that the two methoxycarbyne groups are now placed over one of the Mo−Ru edges in an almost perfect *transoid* arrangement [torsion angle C(2)−Mo(2)−Ru−C(4) = 167°] while one of

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(30) Jeffery, J. C.; Ruiz, M. A. ; Stone, F. G. A. *J. Organomet. Chem.* **1988**, *355*, 231, and references therein.

(31) Alvarez, M. A.; García, M. E.; Martínez, M. E.; Ruiz, M. A. Unpublished results.

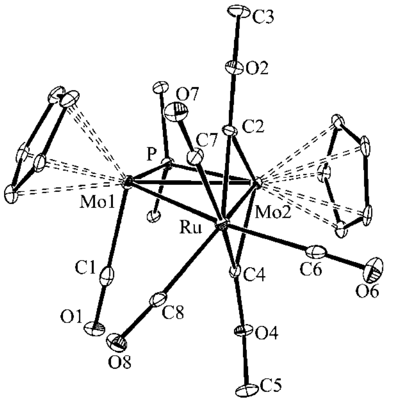

Figure 6. ORTEP diagram (30% probability) of compound **7**. Cy rings (except the C^1 atoms) and H atoms are omitted for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for compound 7

Mo(1)−Mo(2)	2.686(1)	Ru−C(8)	1.952(5)
Mo(1)−Ru	2.813(1)	C(2)−O(2)	1.333(6)
Mo(2)−Ru	2.846(1)	C(4)−O(4)	1.306(6)
Mo(1)−C(1)	2.004(5)	Mo(1)−Mo(1)−Ru	61.0(1)
Mo(2)−C(2)	1.954(5)	Mo(1)−Ru−Mo(2)	56.7(1)
Mo(2)−C(4)	2.005(5)	Mo(1)−P−Mo(2)	67.7(1)
Ru−C(2)	2.091(5)	C(1)−Mo(1)−P	93.3(2)
Ru−C(4)	2.045(5)	C(2)−Mo(2)−P	101.1(2)
Ru−C(6)	1.934(5)	C(4)−Mo(2)−P	104.9(2)
Ru−C(7)	1.966(5)	C(7)−Ru−C(2)	82.2(2)

the carbonyls of the entering $Ru(CO)_4$ fragment has been transferred to the Mo(1) center. The Mo(1)−Mo(2) bond distance, 2.686(1) Å, is significantly shorter than those previously found for single Mo−Mo bonds in related trinuclear clusters, such as the trimolybdenum complex $[Mo_3Cp_3(\mu\text{-}PCy_2)(\mu_3\text{-}CO)(CO)_4]$ (ca. 3.1 Å).[32] In fact, this distance is even shorter than those measured for doubly bonded binuclear species such as the bis(diphenylphosphide) complex $[Mo_2Cp_2(\mu\text{-}PPh_2)_2(CO)_2]$ (2.713(1) Å)[33] and comparable to those measured in our 32-electron complexes **2**, **4**, and **5a**. All this suggests that the electronic unsaturation of the trinuclear cluster is essentially localized on this pair of metal atoms. Yet, the Mo−Ru separations, 2.813(1) and 2.846(1) Å, are also somewhat shorter than those measured in related compounds having Mo−Ru single bonds (2.90–3.1 Å),[34] perhaps as an effect of the positive charge of cluster. The coordination sphere of the molybdenum centers is completed by one Cp ligand and the dicyclohexylphosphide ligand bridging the Mo−Mo edge. This latter ligand exhibits a slightly asymmetric coordination mode, being placed ca. 0.05 Å closer to Mo(1), doubtless as a consequence of the different coordination numbers around the Mo atoms. On the other hand, the methoxycarbyne ligands display slightly different coordination modes; thus, the bridgehead carbon atom C(4) exhibits an almost perfect and rather symmetrical μ_2-coordination mode (Mo(2)−C(4) 2.005(5) Å and Ru−C(4) 2.045(5) Å), whereas the C(2) atom exhibits a more asymmetric coordination (Mo(2)−C(2) 1.954(5) Å and Ru−C(2) 2.091(5) Å), with the Mo(1)−C(2) distance of 2.426(5) Å being indicative of the presence of a further, weak semibridging interaction with the third metal atom.

The spectroscopic data in solution for compound **7** (Table 1 and Experimental Section) are essentially consistent with its solid-state structure. Thus, the IR spectrum exhibits four C−O stretching bands, three of them being characteristic of a pyramidal $Ru(CO)_3$ fragment [2071 (vs), 2026 (s), and 1996 (s) cm^{-1}], while the fourth band, at lower frequency [1956 (w) cm^{-1}], can be associated to the Mo-bound carbonyl ligand. The ^{31}P spectrum exhibits a quite deshielded resonance (200.5 ppm), with a shift in the range of those previously reported by us for related 46-electron heterometallic Mo_2M clusters exhibiting $Mo_2(\mu\text{-}PCy_2)$ moieties (ca. 160–210 ppm).[32] The ^1H and ^{13}C NMR spectra reflect the great asymmetry of the cation by exhibiting independent resonances for the inequivalent Cp and COMe ligands. The latter give rise to characteristic highly deshielded ^{13}C NMR resonances (385.2 and 375.0 ppm), with shifts somewhat higher than those previously reported for the isoelectronic alkylcarbyne cluster $[Mo_2RuCp_2(\mu_3\text{-}CR)(\mu\text{-}PPh_2)(CO)_5]$ [R = Me (350.8 ppm), Et (363.5 ppm)].[34c] This can be due both to the different electron-withdrawing properties of the alkyl and alkoxyl substituents and to the different coordination modes (μ_2 vs μ_3) of the carbyne ligands.

Concluding Remarks. The high unsaturation of the 30-electron bis(alkoxycarbyne) complexes **1a**,**b** allows them to readily react with simple electron-donor molecules (L) at room temperature to give the corresponding double-addition products. This induces the C−C coupling between both alkoxycarbyne ligands to generate quantitatively the new dialkoxyacetylene complexes of the type $[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_2(OMe)(OR)\}(\mu\text{-}PCy_2)(L)_2]^+$ (R = Me, Et). In the case of the dicarbonyl complex, this coupling process can be fully and quantitatively reversed upon photochemical decarbonylation, even when there is no special weakening effect on the corresponding C−C bond of the coordinated alkyne, according to DFT calculations on both *cis* and *trans* isomers of the alkyne complex. The addition of the 16-electron fragment $Ru(CO)_4$ to the unsaturated compound **1a** can be accomplished though the reaction with $[Ru_3(CO)_{12}]$ under photochemical activation, although no C−C coupling between the carbyne ligands is thus induced, but just their migration from Mo−Mo to Mo−Ru bonds. Removal of a methyl cation from the dicarbonyl alkyne-bridged complexes renders initially an unstable $\mu\text{-}\eta^2\text{:}\eta^2$-ketenyl complex, which, according to our DFT calculations, would rapidly rearrange into a $\mu\text{-}\eta^1\text{:}\eta^1$-ketenyl intermediate, which in turn undergoes a fast 1,2-shift of the methoxyl group to generate a new 2-methoxy-2-oxo-ethylidyne bridging ligand. The computed activation barrier for the methoxyl shift is only 78 kJ mol^{-1}, which is in agreement with our inability to detect spectroscopically any intermediates in the experimental reaction. This facile migration process might be a characteristic property of the alkoxyl (as opposed to alkyl or aryl) groups.

Experimental Section

General Procedures and Starting Materials. All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures and distilled prior to use.[35] Petroleum ether refers to that fraction distilling in the range 338–343 K. The compounds $[Mo_2Cp_2(\mu\text{-}COMe)_2(\mu\text{-}PCy_2)]BF_4$ (**1a**) and $[Mo_2Cp_2(\mu\text{-}COEt)(\mu\text{-}COMe)(\mu\text{-}PCy_2)]BF_4$ (**1b**) were prepared

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[32] Alvarez, C. M.; Alvarez, M. A.; García, M. E.; Ramos, A.; Ruiz, M. A.; Graiff, C.; Tiripicchio, A. *Organometallics* **2007**, *26*, 321.

[33] Adatia, T.; McPartlin, M.; Mays, M. J.; Morris, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1989**, 1555.

[34] (a) Khorasani-Motlagh, M.; Safari, N.; Pamplin, C. B.; Patrick, B. O.; James, B. R. *Can. J. Chem.* **2006**, *84*, 330. (b) Bridgeman, A. J.; Mays, M. J.; Woods, A. D. *Organometallics* **2001**, *20*, 2076. (c) Adams, H.; Bailey, N. A.; Gill, L. J.; Morris, M. J.; Sadler, N. D. *J. Chem. Soc., Dalton Trans.* **1997**, 3041.

[35] Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heinemann: Oxford, UK, 2003.

as described previously.[1] Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K) or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. Commercial aluminum oxide (Aldrich, activity I, 150 mesh) was degassed under vacuum prior to use. The latter was mixed under nitrogen with the appropriate amount of water to reach the activity desired. All other reagents were obtained from the usual commercial suppliers and used as received. IR stretching frequencies were measured in solution or Nujol mulls and are referred to as ν (solvent) or ν (Nujol) respectively. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.50 (^{31}P{^{1}H}), or 75.47 MHz (^{13}C{^{1}H}) at 290 K in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). Coupling constants (J) are given in Hz.

Preparation of [Mo$_2$Cp$_2${μ-η^2:η^2-C$_2$(OMe)$_2$}(μ-PCy$_2$)(CN^{t}Bu)$_2$]BF$_4$ (2). A solution of compound **1a** (0.100 g, 0.144 mmol) in dichloromethane (10 mL) was stirred with ^{t}BuNC (40 μL, 0.353 mmol) for 5 min to give a red solution. The solvent was then removed under vacuum, and the residue was washed with petroleum ether to give compound **2** as a red powder (0.116 g, 94%). The crystals used in the X-ray study were grown by slow diffusion of petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{36}H_{56}BF_4Mo_2N_2PO_2\cdot CH_2Cl_2$: C, 47.10; N, 2.96; H, 6.19. Found: C, 47.16; N, 2.99; H, 6.23. ^{1}H NMR (300.13 MHz): δ 5.35 (s, 10H, Cp), 3.92 (s, 6H, OMe), 1.16 (s, 18H, ^{t}Bu), 2.0–1.2 (m, 22H, Cy). ^{13}C{^{1}H} NMR: δ 160.3 (d, J_{CP} = 10, CN), 147.4 (s, μ-CC), 90.9 (s, Cp), 62.4 (s, OMe), 58.7 [s, C^1(^{t}Bu)], 50.0 [d, J_{CP} = 18, C^1(Cy)], 34.7 [d, J_{CP} = 4, C^{2,6}(Cy)], 33.4 [s, C^{6,2}(Cy)], 30.3 [s, C^2(^{t}Bu)], 28.4 [d, J_{CP} = 12, C^{3,5}(Cy)], 28.3 [d, J_{CP} = 10, C^{5,3}(Cy)], 26.4 [s, 2 × C^4(Cy)].

Preparation of [Mo$_2$Cp$_2${μ-η^2:η^2-C$_2$(OMe)$_2$}(μ-PCy$_2$)(CO)$_2$]BF$_4$ (3a). A solution of compound **1a** (0.100 g, 0.144 mmol) in dichloromethane (10 mL) was stirred at room temperature in a high-pressure reactor under a CO atmosphere (60 bar) for 12 h. After depressurization of the reactor, the red resulting solution was transferred into a Schlenk flask. Petroleum ether was then added, the solvents were removed under vacuum, and the residue was then washed with petroleum ether to yield compound **3a** as a red microcrystalline solid (0.101 g, 94%). Upon dissolution of this solid in dichloromethane, the presence of the major isomer *trans*-**3a** along with a small amount of the isomer *cis*-**3a** can be detected by ^{1}H or ^{31}P NMR spectroscopy. After ca. 3 h at room temperature, an equilibrium ratio *trans*-**3a**/*cis*-**3a** of ca. 8 is reached. Anal. Calcd for $C_{28}H_{38}BF_4Mo_2O_4P\cdot CH_2Cl_2$: C, 41.80; H, 4.83. Found: C, 41.68; H, 5.25. Spectroscopic data for *trans*-**3a**: ^{1}H NMR: δ 5.93 (s, 10H, Cp), 3.95 (s, 6H, OMe), 2.4–1.1 (m, 22H, Cy). ^{13}C{^{1}H} NMR: δ 217.1 (d, J_{CP} = 12, CO), 151.3 (d, J_{CP} = 3, μ-CC), 94.2 (s, Cp), 64.3 (s, OMe), 47.5 [d, J_{CP} =20, C^1(Cy)], 34.9 [d, J_{CP} = 4, C^{2,6}(Cy)], 33.0 [s, C^{6,2}(Cy)], 27.9 [d, J_{CP} = 12, C^{3,5}(Cy)], 27.8 [d, J_{CP} = 20, C^{5,3}(Cy)], 25.9 [s, C^4(Cy)]. Data for *cis*-**3a**: ^{1}H NMR: δ 5.71 (s, 10H, Cp), 4.00 (s, 3H, OMe), 3.99 (s, 3H, OMe). ^{13}C{^{1}H} NMR: δ 92.5 (s, Cp), 63.0, 62.9 (2 × s, 2 × OMe); other resonances of this minor isomer were masked by those of the major isomer.

Preparation of [Mo$_2$Cp$_2${μ-η^2:η^2-C$_2$(OEt)(OMe)}(μ-PCy$_2$)(CO)$_2$]BF$_4$ (3b). The procedure is identical to that described for **3a**, but using compound **1b** (0.100 g, 0.142 mmol) instead. This gives compound **3b** (0.100 g, 93%) as a red microcrystalline solid. Upon dissolution of this solid in dichloromethane, the presence of small amounts of the isomers *cis*-**3b** and *cis*-**3b′** can be detected by ^{1}H or ^{31}P NMR spectroscopy. After ca. 3 h at room temperature, an equilibrium ratio *trans*-**3b**/*cis*-**3b**/*cis*-**3b′** of ca. 20/1/1 is reached. Anal. Calcd for $C_{29}H_{40}BF_4Mo_2PO_4$: C, 45.69; H, 5.29. Found: C, 45.77; H, 5.29. Spectroscopic data for *trans*-**3b**: ^{1}H NMR: δ 5.92 (s, 10H, Cp), 4.30 (q, J_{HH} = 7, 2H, OCH$_2$), 3.92 (s, 3H, OMe), 2.5–1.1 (m, 22H, Cy), 1.40 (t, J_{HH} = 7, 3H, Me). ^{13}C{^{1}H} NMR: δ 217.2, 217.1 (2 × d, J_{CP} = 12, 2 × CO), 150.7, 149.8 (2 × d, J_{CP} = 3, 2 × μ-CC), 94.1, 94.0 (2 × s, 2 × Cp), 74.1 (s, OCH$_2$), 64.1 (s, OMe), 47.4, 47.0 [2 × d, J_{CP} =20, 2 × C^1(Cy)], 34.7 [s, C^{2,6}(Cy)], 32.7 [d, J_{CP} = 5, C^{6,2}(Cy)], 27.7 [d, J_{CP} = 11, C^{3,5}(Cy)], 27.6 [d, J_{CP} = 11, C^{5,3}(Cy)], 25.8 [s, 2 × C^4(Cy)], 15.5 (s, Me). Data for *cis*-**3b** and *cis*-**3b′**: ^{1}H NMR: δ 5.85 (s, 10H, Cp). ^{13}C{^{1}H} NMR: δ 92.5, 92.4 (2 × s, 2 × Cp).

Preparation of [Mo$_2$Cp$_2${μ-η^2:η^2-C$_2$(OMe)$_2$}(μ-PCy$_2$)(μ-tedip)]BF$_4$ (4). Compound **1a** (0.050 g, 0.072 mmol) and tedip (30 μL, 0.123 mmol) were stirred in dichloromethane (10 mL) for 24 h in a bulb equipped with a Young's valve. After removal of solvents under vacuum, dichloromethane (10 mL) and petroleum ether (5 mL) were added. Removal of the solvents from the latter mixture under vacuum and washing of the residue with petroleum ether gave compound **4** as a brown powder (0.064 g, 93%). The crystals used in the X-ray study were grown by slow diffusion of petroleum ether into a tetrahydrofuran solution of the complex at 253 K. Anal. Calcd for $C_{34}H_{58}BF_4Mo_2O_7P_3$: C, 42.97; H, 6.15. Found: C, 42.85; H, 5.97. ^{1}H NMR: δ 5.45 (s, 10H, Cp), 4.18 (s, 3H, OMe), 4.09 (s, 4H, OCH$_2$), 3.94 (m, 4H, OCH$_2$), 2.75 (s, 3H, OMe), 2.5–0.4 (m, 22H, Cy), 1.25 (t, J_{HH} = 7, 6H, Me), 1.22 (t, J_{HH} = 7, 6H, Me). ^{31}P{^{1}H} NMR: δ 164.9 (t, J_{PP} = 22, μ-PCy$_2$), 159.7 (d, J_{PP} = 22, μ-tedip). ^{13}C{^{1}H} NMR: δ 158.1 (td, J_{CP} = 12, 2, μ-CC), 117.0 (td, J_{CP} = 28, 3, μ-CC), 90.9 (s, Cp), 64.9 (ft, AXX′, $J_{HP} + J_{HP'}$ = 9, OCH$_2$), 62.7 (ft, AXX′, $J_{HP} + J_{HP'}$ = 12, OCH$_2$), 60.2, 59.9 (2 × s, 2 × OMe), 53.8 [d, J_{CP} = 23, C^1(Cy)], 46.1 [d, J_{CP} = 14, C^1(Cy)], 34.8, 33.8 [2 × s, 2 × C^2(Cy)], 28.3, 27.8 [2 × d, J_{CP} = 11, 2 × C^3(Cy)], 26.3, 26.0 [2 × s, 2 × C^4(Cy)], 16.3, 16.1 (2 × s, 2 × Me).

Preparation of [Mo$_2$Cp$_2${μ-C(CO$_2$Me)}(μ-PCy$_2$)(CO)$_2$] (5a). Neat 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 20 μL, 0.134 mmol) was added to a dichloromethane solution (10 mL) of compound **3a** (0.090 g, 0.120 mmol), and the mixture was stirred for 10 min to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with CH_2Cl_2–petroleum ether (1:2), and the extracts were chromatographed on alumina (activity IV, 20 × 3 cm) at 253 K. Elution with dichloromethane–petroleum ether (3:1) gave an orange fraction. Removal of solvents from this fraction gave compound **5a** as an orange powder (0.049 g, 63%). The crystals used in the X-ray study were grown by cooling at 253 K a saturated petroleum ether solution of the complex. Anal. Calcd for $C_{27}H_{35}Mo_2O_4P$: C, 50.16; H, 5.46. Found: C, 50.22; H, 5.40. ^{1}H NMR (C_6D_6): δ 5.27 (s, 10H, Cp), 4.02 (s, 3H, OMe), 2.5–1.1 (m, 22H, Cy). ^{13}C{^{1}H} NMR (C_6D_6): δ 402.8 (br, s, μ-C), 221.4 (d, J_{CP} = 11, CO), 191.8 (s, *C*=O), 91.5 (s, Cp), 50.9 (s, OMe), 45.4 [d, J_{CP} = 18, C^1(Cy)], 36.1 [s, C^{2,6}(Cy)], 34.3 [s, C^{6,2}(Cy)], 28.4 [d, J_{CP} = 12, C^{3,5}(Cy)], 28.2 [d, J_{CP} = 12, C^{5,3}(Cy)], 26.5 [s, C^4(Cy)].

Reaction of 3b with DBU. Neat 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 20 μL, 0.134 mmol) was added to a dichloromethane solution (10 mL) of compound **3b** (0.050 g, 0.066 mmol), and the mixture was stirred for 10 min to give an orange solution. The solvent was then removed under vacuum, the residue was extracted with CH_2Cl_2–petroleum ether (1:2), and the extracts were chromatographed on alumina (activity IV, 20 × 3 cm) at 253 K. Elution with dichloromethane–petroleum ether (3:1) gave an orange fraction, this containing a 5:4 mixture of compounds **5a** and [Mo$_2$Cp$_2${μ-C(CO$_2$Et)}(μ-PCy$_2$)(CO)$_2$] (**5b**), respectively. Spectroscopic data for compound **5b**: ^{1}H NMR (C_6D_6): δ 5.30 (s, 10H, Cp), 4.73, 4.55 (ABX$_3$, J_{AB} = 10, J_{AX} = J_{BX} = 7, 2H, OCH$_2$), 1.37 (t, J_{HH} = 7, 3H, Me), 2.5–1.2 (m, 22H, Cy). ^{13}C{^{1}H} NMR (C_6D_6): δ 403.3 (s, μ-C), 221.5 (d, J_{CP} = 7, CO), 191.3 (s, C=O), 91.5 (s, Cp), 59.6 (s, OCH$_2$), 45.4 [d, J_{CP} = 18, C^1(Cy)], 36.1 [s, C^{2,6}(Cy)], 34.3 [s, C^{6,2}(Cy)], 28.4 [d, J_{CP} = 12, C^{3,5}(Cy)], 28.2 [d, J_{CP} = 12, C^{5,3}(Cy)], 26.5 [s, C^4(Cy)], 15.8 (s, CH$_3$).

Preparation of [Mo$_2$Cp$_2${μ-C(CO$_2$Me)}(μ-PCy$_2$)(μ-CO)] (6). A toluene solution (10 mL) of compound **5a** (0.050 g, 0.077 mmol) was irradiated with visible—UV light for 30 min in a Pyrex-jacketed

Schlenk tube refrigerated by water, while keeping a gentle N_2 purge. Solvent was removed under vacuum from the brown-reddish resulting solution, the residue was then extracted with dichloromethane−petroleum ether (1:1), and the extracts were filtered through diatomaceous earth. Removal of the solvents from the filtrate yielded compound **6** as a red powder (0.037 g, 78%). Anal. Calcd for $C_{26}H_{35}Mo_2O_3P$: C, 50.50; H, 5.70. Found: C, 50.44; H, 5.65. ^1H NMR: δ 5.96 (s, 10H, Cp), 3.57 (s, 3H, OMe), 1.9–0.3 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 361.1 (d, $J_{CP} = 15$, μ-C), 299.5 (d, $J_{CP} = 11$, μ-CO), 180.2 (s, C=O), 96.1 (s, Cp), 51.4 (s, OMe), 41.7, 40.2 [2 × d, $J_{CP} = 18$, 2 × C^1(Cy)], 33.3, 32.6 [2 × s, 2 × C^2(Cy)], 27.3 [d, $J_{CP} = 13$, C^3(Cy)], 27.1 [d, $J_{CP} = 12$, C^3(Cy)], 25.9 [s, 2 × C^4(Cy)].

Preparation of $[Mo_2RuCp_2(\mu\text{-COMe})_2(\mu\text{-PCy}_2)(CO)_4]BF_4$ (7). A tetrahydrofuran solution (10 mL) of compound **1a** (0.040 g, 0.058 mmol) and $[Ru_3(CO)_{12}]$ (0.017 g, 0.027 mmol) was irradiated with visible−UV light for 2.5 h in a Pyrex-jacketed Schlenk tube refrigerated by water, while keeping a gentle N_2 purge. Solvent was removed under vacuum from the green-brownish resulting solution, and the residue was washed with petroleum ether (5 × 20 mL). This solid was then dissolved in dichloromethane (10 mL) and filtered through diatomaceous earth. Petroleum ether (10 mL) was then added to the filtrate, and the solvents were removed under vacuum to give compound **7** as a green solid (0.038 g, 72%). The crystals used in the X-ray diffraction study were grown by slow diffusion of a layer of diethyl ether into a dichloromethane solution of the complex at 253 K. Anal. Calcd for $C_{30}H_{38}BF_4Mo_2O_6PRu$: C, 39.80; H, 4.23. Found: C, 39.87; H, 4.32. ^1H NMR: δ 5.60, 5.58 (2 × s, 2 × 5H, 2 × Cp), 4.52, 3.99 (2 × s, 2 × 3H, 2 × OMe), 2.1–1.0 (m, 22H, Cy). $^{13}C\{^1H\}$ NMR: δ 385.2, 375.0 (2 × d, 2 × $J_{CP} = 4$, 2 × μ-COMe), 228.9 (s, MoCO), 199.7 (s, RuCO), 197.1 (s, 2 × RuCO), 94.7, 92.3 (2 × s, 2 × Cp), 76.5, 70.5 (2 × s, 2 × OMe), 49.0 [d, $J_{CP} = 22$, C^1(Cy)], 43.5 [d, $J_{CP} = 15$, C^1(Cy)], 35.8, 34.3 [2 × s, 2 × C^2(Cy)], 32.0 [s, br, 2 × C^2(Cy)], 28.0–27.0 [m, 4 × C^3(Cy)], 26.20, 26.15 [2 × s, 2 × C^4(Cy)].

Computational Details. All computations were carried out using the GAUSSIAN03 package,[36] in which the hybrid method B3LYP was applied with the Becke three-parameter exchange functional[37] and the Lee–Yang–Parr correlation functional.[38] Effective core potentials (ECP) and their associated double-ζ LANL2DZ basis set were used for the molybdenum and phosphorus atoms,[39] supplemented by an extra d-polarization function in the case of P.[40] The light elements (O, C, and H) were described with 6-31G*.[41] Geometry optimizations were performed under no symmetry restrictions using initial coordinates derived from X-ray data, when possible, and frequency analyses were performed to ensure that minimum structures were achieved with no imaginary frequencies. For the localization of the transition state (**TS-1**) leading to compound **5a**, the Synchronous Transit-Guided Quasi-Newton (STQN) was used, as implemented in the GAUSSIAN03 suite, employing a tight cutoff on forces and step size to determine convergence (keyword Opt=QST2,tight). In all cases, negative frequencies were absent, except for **TS-1**, for which one, and only one, imaginary frequency (466i) was found, as expected for a transition state. Molecular orbitals and frequencies were visualized using the Molekel[42] program. The topological analysis of the electron density was carried out using the Xaim routine.[43]

X-ray Structure Determination of Compounds 4 and 5a. Data were collected on a Smart-CCD-1000 Bruker diffractometer using graphite-monochromated Mo-Kα radiation at 100 K (for **4**) and 120 K (for **5a**). Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in three sets of 30 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART[44] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT,[44] and a multiscan absorption correction was applied with SADABS.[45] Using the program suite WinGX,[46] the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[47] For compound **4**, there are two independent molecules in the asymmetric unit, both displaying similar structural parameters; one of the cyclohexyl rings and two ethoxyl groups (of the tedip ligand) were found to be disordered in two sites. All the nonhydrogen atoms were refined anisotropically, whereas the hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. The cyclohexyl ligand could be modeled in two positions with stably refined populations of ratio 40:60, which were fixed for final refinement. Similarity restraints were used for the two disordered components, and fixed positional parameters were imposed for the minor component. For the ethoxyl groups a similar scheme was employed, and during final refinements a possible molecule of a solvent (most probably THF) was found to be present in the asymmetric unit. Therefore, the SQUEEZE[48] program, as implemented in PLATON,[49] was used to model the corresponding electron densities. After convergence, the strongest residual peaks (1.17–0.96 e Å^{-3}) were located around the disordered cyclohexyl group. The refinement converged with the residuals shown in Table 8. For compound **5a** all non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were fixed at calculated geometric positions in the last least-squares refinements, with a given isotropic thermal factor. One of the Cp ligands and one of the cyclohexyl groups were disordered over two positions. The populations of the two congeners refined stably to a 37:63 (for the Cp) and 40:60 (for the cyclohexyl) ratios. Rigid-bond restraints[50] and isotropic restraints were placed on the anisotropic displacement

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(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R. ,Montgomery,J. A., Jr.; Vreven, T.; Kudin, K. N. Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao,O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T. ; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.02;* Gaussian, Inc.: Wallingford, CT, 2004.

(37) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(38) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(39) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(40) Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K. F.; Stegman, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237.

(41) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Petersson, G. A.; Al-Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081. (c) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193.

(42) Portmann, S.; Lüthi, H. P. *MOLEKEL*: An Interactive Molecular Graphics Tool. *CHIMIA* **2000**, *54*, 766.

(43) Ortiz J. C.; Bo, C. *Xaim*; Departament de Química Física i Inorgànica (Universidad Rovira i Virgili): Tarragona, Spain, 1998.

(44) *SMART & SAINT* Software Reference Manuals, Version 5.051 (Windows NT Version); Bruker Analytical X-ray Instruments: Madison, WI, 1998.

(45) Sheldrick, G. M., *SADABS, Program for Empirical Absorption Correction*; University of Göttingen: Germany, 1996.

(46) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(47) Sheldrick, G. M., *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(48) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *A46*, 194.

(49) (a) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *A46*, C34. (b) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1998.

(50) Hirshfeld, F. L. *Acta Crystallogr., Sect. A* **1976**, *32*, 239.

Table 8. Crystal Data for Compounds 4, 5a, and 7

	4	5a	7
mol formula	$C_{34}H_{58}BF_4Mo_2O_7P_3$	$C_{27}H_{35}Mo_2O_4P$	$C_{31}H_{40}BCl_2F_4Mo_2O_6PRu$
mol wt	950.43	646.40	990.26
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
radiation (λ, Å)	0.71073	0.71073	0.71073
a, Å	11.967(2)	9.819(2)	17.9342(9)
b, Å	19.929(4)	11.145(2)	14.7605(5)
c, Å	20.267(4)	12.932(3)	13.5710(7)
α, deg	62.708(4)	73.307(4)	90
β, deg	76.801(4)	76.161(3)	99.491(2)
γ, deg	75.315(4)	86.211(3)	90
V, Å^3	4119.6(13)	1316.2(5)	3543.3(3)
Z	4	2	4
calcd density, g cm^{-3}	1.532	1.631	1.856
absorp coeff, mm^{-1}	0.786	1.044	1.377
temperature, K	120(2)	100.0(1)	100.1(2)
θ range (deg)	1.14–26.43	1.69–26.41	0.41–25.68
index ranges (h, k, l)	−14, 14; −18, 24; 0, 25	−11, 12; −13, 13; 0, 16	0, 21; −17, 0; −16, 16
no. of reflns collected	22564	14549	19960
no. of indep reflns (R_{int})	15289 (0.0411)	5357 (0.0344)	6369 (0.0453)
no. of reflns with $I > 2\theta(I)$	9369	4145	4621
R indexes	$R_1 = 0.0496$	$R_1 = 0.0506$	$R_1 = 0.0361$
[data with $I > 2\sigma(I)$]^a	$wR_2 = 0.1075^b$	$wR_2 = 0.119^c$	$wR_2 = 0.0807^d$
R indexes (all data)^a	$R_1 = 0.1001$ $wR_2 = 0.1225^b$	$R_1 = 0.0671$ $wR_2 = 0.1262^c$	$R_1 = 0.0599$ $wR_2 = 0.0952^d$
GOF	0.923	1.064	1.061
no. of restraints/params	39/990	46/395	0/435
$\Delta\rho$ (max., min.), e Å^{-3}	0.914, −1.38	2.293, −1.178	1.049, −1.072

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. ^{b} $a = 0.0597$, $b = 0$. ^{c} $a = 0.0500$, $b = 5.6363$. ^{d} $a = 0.0481$, $b = 0$.

parameters of the minor components. The refinement converged with the residuals shown in Table 8.

X-ray Structure Determination of Compound 7. Data collection for compound **7** was performed at 100(2) K on a Nonius Kappa CCD single diffractometer, using graphite-monochromated Mo Kα radiation. Images were collected at a 29 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and 50 s exposure time per image. Data collection strategy was calculated with the program Collect.[51] Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.[52] A semiempirical absorption correction was applied using the program SORTAV.[53] Using the program suite WinGX,[46] the structure was solved by Patterson interpretation and phase expansion and refined with full-matrix least-squares on F^2 with SHELXL97.[47] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at calculated positions and were given an overall isotropic thermal parameter. Crystallographic data and structure refinement details for compound **7** are collected in Table 8.

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Supporting Information Available: Tables of selected molecular orbitals for complexes *trans*-**3a** and *cis*-**3a** (pdf) and a CIF file containing the crystallographic data for the structural analysis of compounds **4**, **5a**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(51) *Collect*, data collection software; Nonius B. V.: The Netherlands, 1997–2004.

(52) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(53) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.